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EXPERIMENTS WITH THE BLACK GLAZE ON GREEK VASES

THE nature and constitution of the shining, black, decorating medium from which Greek vases derive so much of their character have been the subject of discussion for over a century, and, according to a recent writer,[1] offer a still unsolved problem. This view I hope to disprove. What had been done up to 1879 toward determining the nature of the glaze is summarized by Blümner,[2] to whose work I have had recourse in many instances because of my inability to reach some of the books in which these results originally appeared.

The earliest investigations, undertaken with a view to discovering the composition of the Greek glaze, were those of Caylus in 1761.[3] According to him the glaze was made of a very ferruginous earth, which he classifies as manganese. This earth, which baked red, could be rendered black, he claimed, by an admixture of color, or other earths.[4] According to Blümner[5] various later authorities have advanced theories that the materials producing the glaze might be graphite and burnt magnesia, that the gloss is due to some glassy lava helped out by a salt, that the glaze is not made up of a metal but an earth, that a carbon, or a combination of iron oxide and manganese oxide, may have furnished the black, and, finally, that the component parts of the glaze are oxide of manganese and an alkaline silicate. But in spite of all these views Blümner claimed that the nature of the black color had not been finally

[1] H. B. Walters, *History of Ancient Pottery*, I, pp. 214 and 220. See, *contra*, Brongniart, *Traité des Arts Céramiques*, I, p. 549, where the claim is made that the question is solved.

[2] *Technologie und Terminologie der Gewerbe und Künste bei Griechen und Römern*, II, pp. 74 ff.

[3] *Recueil d'Antiquités*, I, pp. 86–87.

[4] Caylus, *op. cit.* I, pp. 86–87.

[5] *Op. cit.* II, pp. 76–77.

determined. It was his opinion also that Birch (*Anc. Pot.* p. 175) was not necessarily correct in believing that an alkali, such as potash or soda, iron oxide, and chalk were the chief ingredients, for the amount of iron discovered by that scholar was no greater in the glaze than in the clay itself.[1] As to the glossy nature of this decorating medium he admits that, while it never has the character of a glaze but always of a varnish, microscopic examination shows that the black color has melted together with the surface of the vase.[2] The melting, according to this same scholar, was due to the fusing of a varnish (*Firniss*) with which both bare clay and black medium were covered.[3] Nevertheless, Blümner sharply distinguished between this varnish and the transparent glaze employed by the Romans, and stated that the Greek wares are never glazed.[4] On the other hand, he believed that the black itself must have been more or less of a varnish. To produce this glaze,[5] according to the same writer,[6] John found by analysis and synthesis that the ancients used alkaline substances and salt. For this purpose soda, saltpeter, common salt, borax, glass, or boracic acid could have been used.

Of all the earlier experiments conducted with a view to solving the question of the make-up of the glaze those of Salvétat at the Sèvres potteries appear to be the most worthy of attention. His experiments[7] showed that the glaze contained silica, alumina, oxide of iron, chalk, magnesia, and alkali. In a further discussion of the glaze Brongniart states[8] that the indispensable elements of its composition are oxide of iron and oxide of manganese, and that its fusibility is due to some alkaline silicate. In his attempts to reproduce the glaze Salvétat found that, by taking carbonate of soda, sand, and chalk, he was able to make a flux, and that by mixing with it in varying quantities a combination in equal parts of oxide of iron and

[1] Blümner, *op. cit.* II, p. 78. [2] *Op. cit.* II, p. 75.

[3] *Op. cit.* II, p. 76; also p. 89. The same view was held by Birch, *Hist. of Anc. Pot.* p. 174, and by Brongniart, *Traité*, I, p. 561.

[4] *Op. cit.* II, p. 89.

[5] In describing this medium I use the word "glaze" in preference to "varnish" for reasons which will be apparent later.

[6] *Op. cit.* II, p. 90. [7] Brongniart, *op. cit.* I, p. 550.

[8] *Op. cit.* I, pp. 551, 552.

manganese he obtained a black glaze capable of fusing at about the melting point of pure gold.[1] The glaze, however, as he composed it, contained manganese, which is absent from the tabulated results of his analyses. He claims to have found it present in some black glaze. Its presence,[2] indeed, he believed was not accidental, but due to intentional introduction by the painter. The incorrectness of this belief I shall show later.

Among the later writers Walters[3] distinguishes between a glaze which was applied to the surface before the laying on of what he calls the black varnish, and the black varnish itself. This view approximates those of Birch, Blümner, and Brongniart,[4] who consider the black and the glaze different from each other. Lastly, Furtwängler and Reichhold[5] are of the opinion that the black glaze is apparently made up of two parts, a thin, reddish, shining, flowing material and some substance, which by firing gives the black.

To summarize, then, one group of writers have held that the glaze is a coating independent from the black, the other that both the glaze and the black entered into the make-up of the black lustre. In the latter case the opinions were that the material was artificially compounded; in the former, presumably, some silicate was in mind as the material furnishing the gloss.

It is not likely that the glaze is furnished by a material separate from the black. Had the vases been coated with a glaze previously, or subsequently, to the application of the color, the red clay ground would have presented the same hard, glossy surface as the black, and would resist scratching in the same manner as the black. But such is not the case — at least, in vases which I have examined. Invariably, while the blade of a knife would slip over the black glaze without effect, its application to the red clay ground occasioned scratches. This in itself showed that the gloss of the red ground was not due to a glaze which covered the vase; and an examination of various specimens of red-figured ware under a powerful microscope failed to reveal the presence of a glaze on the clay

[1] Brongniart, *op. cit.* II, p. 554. [2] Brongniart, *op. cit.* II, p. 551.
[3] *Hist. of Anc. Pot.* I, pp. 214 and 219. [4] Blümner, *op. cit.* II, pp. 90, 91.
[5] *Griechische Vasenmalerei*, Series I, Text, p. 19.

ground. On the other hand, such microscopic examination did demonstrate that the black coloring-matter was a glaze, for under the glass one could distinctly see the fused state of the lustre.

Being thus convinced that the Greek potter (or painter) decorated his vases with a material which was in itself a glaze, it remained, first, to find out, if possible, what composed this glaze, and, secondly, to confirm the discovery by synthesis. At the outset of this investigation it seemed that the glaze could not have been of a complicated nature, and, therefore, difficult of composition. Its character remained constant through too many generations of potters, and was in use over too wide a territory to allow an over-nice adjustment of proportions or of materials. It seemed rational for that reason to assume as simple a composition as possible.

While studying the different analyses of Greek clays which have appeared[1] from time to time in various places, I was impressed with the fact that not only were the constituent parts constant, but that the same constancy was also to be observed in the proportions in which these parts entered into the make-up of the clay. In other words, the clay in the Greek vases, although they are found in widely scattered localities, is practically the same throughout — it is a constant. Besides marking this constancy in the materials composing the clay, I also noted that the elements which, according to Salvétat's analysis, went to make up the Greek glaze were the same as those which contributed to the composition of the clay — with one addition, and this addition is a large amount of an alkali.[2] Apparently, therefore, the glaze in its essentials was a clay — quite as much so as the clay of the body of the vase — with the addition of soda, which is absent from the clay of the vase, to render it fusible as a glaze.

[1] Brongniart, *op. cit.* I, p. 550; Robinson, *Cat. of Greek and Roman Vases*, Museum of Fine Arts, Boston, p. 35; Blümner, *op. cit.* II, p. 56.

[2] The average of Salvétat's, Robinson's, and Blümner's analyses gives the following proportions (see last footnote):

Silica	Alumina	Oxide of Iron	Chalk	Magnesia
56.43	17.48	12.73	7.98	2.92

The average of Salvétat's analyses of glazes (Brongniart, *op. cit.* I, p. 550), is:

Silica	Alumina	Oxide of Iron	Chalk	Magnesia	Alkali
48.15	11.90	11.85	5.70	2.30	17.10

To discover at what temperature this fusion occurred I had recourse to the electric furnace. For the manipulation of this I am indebted to Professor George A. Hulett of Princeton University. Careful readings showed that pieces of the black glaze, when submitted to the heat of the furnace, retained their color up to 950° centigrade, but that somewhere between that temperature and 1065°, and, according to Professor Hulett, probably nearer to 1065°, the black passed over into red. This showed that the heat employed by the Greek potter could have risen as high as 950°, or a little higher, but could not have reached 1065°. It is interesting to know that approximately 1065° and 950° represent respectively the melting-points of gold and silver, and the idea comes to mind that the Greek potter may have used these metals, much as the modern potter uses cones, to regulate the heat of his kiln.

Having thus determined that the material used for decoration was a glaze, and that the temperature must have been close to 950° centigrade,[1] the next step was to ascertain the nature of the coloring-matter used in the glaze. Salvétat had postulated manganese as an essential, and his tabulated analyses showed an oxide of iron present. Experiments, therefore, had to be conducted in order to determine, first, whether manganese was really present as an artificial element introduced into the glaze by the potter, or whether it was accidental, and, in the second place, whether the iron used was a ferric or ferrous oxide. In clay the coloring material which gives the reddish color is ferric oxide. That the same material should be employed to produce black is unlikely.[2] The settling of these questions I owe to Professor William Foster of Princeton University, who conducted for me a series of delicate chemical experiments.

A fragment weighing 51 grammes from a Greek vase,[3] and covered with black glaze, was placed in a silver crucible, and the glaze fused with caustic potash to remove it from the clay. The melt obtained in this way showed a faint greenish tinge,

[1] The frequency with which reddened glaze appears on Greek vases shows that the temperature ran in the neighborhood of 950°, and also that it probably rose somewhat above that point.

[2] In conjunction with manganese it might be employed to soften the density of the black.

[3] From the American excavations at the Heraeum.

which suggested that a very small percentage of manganese was present. Later a careful test was made for this metal. Meanwhile the melt, as it now stood, contained all the elements of the glaze. These were then separated to a certain extent. To separate the silica the melt was treated with water, and then with dilute nitric acid. Sodium hydroxide was added to alkaline reaction, and the mixture then heated. The precipitate was washed, dissolved in nitric acid, and the solution evaporated to dryness: the silica was dehydrated and separated from the mixture by the use of hydrochloric acid, and then filtered off. Considerable silica was obtained.

The iron still remained in the filtrate. To remove this, sodium carbonate and sodium acetate were used, with the result that a large amount of basic acetate of iron was found present. To determine that the iron obtained did not come from the clay from which the glaze had been dissolved further experiments had to be performed. Ordinary clays contain ferric oxide and usually some ferrous oxide. To prove, therefore, that considerable ferrous oxide, which produces a black, was present in the glaze apart from the clay the following tests were made. A piece of a vase, covered with glaze, was heated together with sulphuric acid and hydrofluoric acid, great care being taken to exclude the air, and the mixture was evaporated to dryness. The residue from this was treated with water and sulphuric acid, and a solution of potassium permanganate was added drop by drop. A considerable quantity of the permanganate was decolorized, showing that the solution of the glaze contained ferrous iron. This, of course, may have been in the clay as well, for both clay and glaze had been treated together. To find out, therefore, whether any came from the clay, a fragment of a vase without glaze was treated by the same process. Ferrous iron was found to be present in a much smaller quantity. It was apparent therefore that most of the ferrous iron was in the glaze.

To get the relative amounts of ferrous iron in the glaze and in the clay this test was made.

Three grammes of clay and glaze were treated with one cubic centimetre of dilute sulphuric acid and five cubic centimetres of a solution of hydrofluoric acid, and the mixture then evapo-

rated to dryness. The residue was then taken up with one cubic centimetre of dilute sulphuric acid and considerable water. This was titrated with a solution of potassium permanganate, when it was found that it required 0.6 cubic centimetre to oxidize the ferrous iron. The same test was applied to an equal amount of the clay without the glaze. To oxidize the iron in this required only 0.2 cubic centimetre of permanganate. There was, therefore, three times as much ferrous iron in the glaze as in the clay.

Finally, to determine whether or not the manganese was an essential component of the glaze, as Salvétat claimed, the original filtrate, from which the iron and silica had been removed, was treated with ammonium hydroxide, filtered, and the solution then treated with hydrogen sulphide. A *very* small, dark precipitate formed, which, when treated in an oxidizing flame by means of a borax bead, gave no color. This made it manifest that manganese was present in the glaze in no appreciable quantity. This test was confirmed by various others, by fusing different quantities of glaze with sodium carbonate and potassium chlorate. By this treatment a greenish color was obtained, thus demonstrating that manganese was present as shown by the first experiment, but only in an exceedingly small quantity. Its occurrence therefore must have been accidental, and in fact the manganese was probably present in the clay.

This series of experiments made it clear that the glaze contained much more iron than the clay, and that manganese was not an *essential* component of the glaze.

With the information thus acquired it was now possible to attempt to show empirically that what the Greeks used for glazing was not altogether an artificial composition, as Salvétat and others have imagined, but merely clay with soda and iron added — the former to help fuse it, and the latter to color it. It seemed of little moment what clay was utilized in the experiments so long as it was as plastic as the Greek clay, for while it might have required less soda to fuse the Greek clay than others, the difference was one of degree, not of principle.

The clay which I used at first in my experiments was one obtained from the potteries at Rocky Hill, N.J., and it came,

I was given to understand, from the Hudson valley. At a low temperature it offers a striking likeness in color and texture to the Greek clay, and at a great heat it fuses after the fashion of the Greek. To this clay I added soda in varying quantities and found that it would fuse into a glaze. But when so fused it had a brownish color even after the addition of ferrous oxide. Indeed when enough iron was introduced to achieve the black, the composition would not fuse because of the preponderance of coloring-matter. It then occurred to me that if I could get a clay which lacked ferric oxide, or, at least, contained it to an inconsiderable degree, — for it was this which caused the red-brown tinge, — I could use much less black coloring-matter, and so obtain a fusible material. I therefore procured some pipe clay which contains very little ferric oxide. There could be nothing forced in using it, for the Greeks employed it on their white lecythi, and, even if we lacked that evidence, its employment would be warranted, for it is found in a fairly pure state in the island of Naxos, and must therefore have been known to the ancients from that quarter.

With this pipe clay I renewed my experiments.[1] In order that the soda, when dissolved in the water with which the ferrous oxide was mixed, should not sink into the clay of the vase, I first fritted it with the pipe clay, and then, after the frit had been reduced to a powder, mixed it with the coloring-matter and applied it to the surface of a piece of baked clay. In order that the coloring-matter, with the flux, might stay in suspension in the water so that it might be applied to the vase with a pen, or brush, gum arabic was mixed with the water. When the piece of clay, thus covered with the mixture, was submitted to the heat of a muffle furnace, it fused and produced a glaze more or less rough, and more or less black, according to the degree of fineness, and the thinness of application, and according to the amount of ferrous oxide used. Not to be tedious by enumerating the number of trials I made before getting the desired result, I may say that it proved eventually that a combination of eight parts of nitrate of soda to one of clay, fritted together, and then mixed in the proportions of two

[1] These experiments occupied me quite steadily from October, 1907, to May, 1908.

parts of frit to one of ferrous oxide, produced a glaze identical with that on the Greek vases.[1]

The testing of this glaze to find out if it would produce a fine line when used with some drawing instrument led to another subject, the question of the instrument used in drawing the relief lines which appear on red-figured vases. Reichhold[2] states that Brunn believed that a drawing pen was employed, that Walters argued for a quill, and that Hartwig thought that a simple feather was used. Reichhold himself at first thought a wooden pencil was employed,[3] but, later in his investigation, settled upon a bristle tied to a handle.[4] That a drawing pen — that is, a pen with adjustable nibs — was used, is not very likely. Such an instrument does not give the peculiar line with a depression in the middle that appears on Greek vases. The possibility of the use of a quill I pass over for a moment. As to Hartwig's idea that a snipe feather was used, long before I undertook my investigation of the nature of the glaze I made experiments with such a feather. In the attempt to get the curious relief line, I used a fairly thick drawing ink, with the purpose of getting as close as possible to the quality of the glaze in the matter of thickness. In using the feather I encountered the same difficulty which Reichhold[5] later met with; namely, that while I could get lines of extreme fineness, I could not get the depressed centre of the Greek lines. It may be possible, though I doubt it, that a feather would produce relief lines if used with such a glaze as I made. With single-pointed instruments, such as a pointed stick, a sharpened quill, and a brush, I could not get the "double-tracked" effect of the Greek artist's lines; and a feather, although it ends in two fine points, acts, in practice, like a single-pointed object, such as a brush. Therefore the difference in medium does not seem to me enough to make the feather possible.

[1] Had the pipe clay been a more fusible variety, the amount of soda used could have been much less.

[2] *Griechische Vasenmalerei*, p. 20. [3] *Op. cit.* p. 23. [4] *Op. cit.* p. 148.

[5] Reichhold, *op. cit.* p. 20. I made my experiments with the feather immediately after the appearance of Hartwig's article in 1899. See *Jb. Arch. I.* 1899, pp. 147 ff.

As to the bristle, with which Reichhold claimed finally to have drawn the relief lines, I must admit I could do nothing. When made long enough to show the flexure of the instrument illustrated on the Boston vase,[1] it slipped about over the surface of the clay in an uncontrollable manner; when short enough to be stiff, it scratched and left no mark. The coloring-matter, whether glaze or ink, collected in drops along the bristle, and did not flow readily. The only way, indeed, in which I could make the bristle leave a line was by pressing on it until it was so bent that much of it trailed along the surface of the clay. But, as I just said, its lack of stiffness made it slip so that I could not trace a design with it. This fact, contrasted with the surety with which the ancient artists' lines begin and end, and describe curves, leads me to think that the bristle cannot be said, with any certainty, to have been the instrument used for drawing the relief lines. The bristle, moreover, did not produce the "double-tracked" lines.

In connection with the Boston vase, Reichhold says[2] that the implement held in the youth's left hand is a glaze-pencil, *Firnissstift*.[3] By this I understand him to mean a pointed stick with which, in his earlier experiments, he claims to have produced the relief lines. It has occurred to me that this object might be merely a vial containing glaze, into which the painter could handily dip his drawing instrument. This, however, cannot be proved. At all events, the object is apparently too short to be used as a pencil.

Having found the pointed stick unsatisfactory and not in correspondence, so far as flexibility goes, with the instrument shown on the Boston vase, and the bristle impossible because of its extreme lightness, flexibility, and inability to distribute the glaze in a flowing manner, I tried an ordinary pen. From this not only did the glaze flow easily, but in several instances it produced a relief line with a depressed centre. In every case the line had considerable elevation from the surface of the clay. With a quill, also, which I whittled into a pen, I produced the same relief lines. It is quite impossible, in fact,

[1] *Jb. Arch. I.* 1899, pl. 4. [2] *Griechische Vasenmalerei*, p. 21.

[3] Walters, *Hist. of Anc. Pot.* p. 228, states that this implement seems to be "the sharp tool for engraving the outlines of the figures."

to draw with the glaze without getting a relief line. The reason lies in the nature of the glaze, and that of the clay to which it is applied. In the first place the glaze is composed of certain insoluble ingredients, such as the particles of silica and ferric oxide, to say nothing of the other elements which contributed to make up the clay from which the glaze in part was made. These particles are of sufficient size to prevent their entrance into the body of the clay to which the glaze is applied. The clay, of course, being more or less porous, sucks in the water of the glaze but acts like a strainer toward the other parts of the glaze, and so keeps them on the surface.

This fact leads me to believe that the view that a line once drawn on a Greek vase could not be removed is incorrect.[1] For all glazes which are to be subjected to fire must be made up largely of insoluble material and so must remain, as mine did, on the surface of the clay. In the case of the glaze which I composed, since it remained entirely on the surface, I was able to remove it easily from the clay surface by simply washing it away with water. There seems to be no reason, therefore, why the Greek glaze could not have been removed in the same manner[2] before firing.

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[1] *Griechische Vasenmalerei*, p. 150.

[2] Why Walters (*op. cit.* I, p. 229) says that the Greek artist was obliged to draw his design on a damp surface, and why the color of the glaze should be confounded with the tint of the clay, I do not see. In the first place, the glaze, at least as I experimented with it, could be used alike on a dry or a wet surface, the only difference being that in the latter case the glaze dried less quickly; in the second place, even were the clay wet, and even were it moist and unbaked, it presented a marked difference in color from the black glaze.